



Feature article

Design of block copolymer micelles via crystallization

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ABSTRACT

This Feature Article provides an overview of the progress made over the last few years in the design of diblock copolymer micelles based on *crystallization-driven self-assembly* (CDSA) towards the development of novel and fascinating morphologies with crystalline-cores. Here, we describe the different approaches employed in order to engineer a large variety of semicrystalline micellar architectures. We highlight kinetic strategies that have been employed to direct morphological transitions, which can then be further tuned thus increasing the range of possible micellar structures. We then emphasize the development of complex hybrid assemblies generated by taking advantage of the self-assembly process of crystalline-corona di-BCP micelles with colloidal particles. Each section introduces and emphasizes the potential applications of this class of nanomaterials.

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1. Introduction

The ability of diblock copolymers (di-BCPs) to spontaneously organize into a wide range of morphologies, including many complex or hierarchical assemblies, has attracted significant attention due to their potential use in the development of nanomaterials with controlled structures and tunable properties for different applications [1,2]. Remarkably, the successful preparation of micelles from crystalline-coil BCPs by crystallization-driven self-assembly (CDSA) showed over the last ten years that semicrystalline BCPs are very appealing candidates for the development of materials with complex architectures. As a matter of fact, the self-assembly or the micellization of non-crystalline BCPs in solution is well-documented and very good agreement has been established between the experimental and theoretical studies [3–14]. Selective solvation gives rise to the formation of micelles with a core consisting of the insoluble block that is surrounded by a corona formed by the soluble block [10,15]. The resulting structures will depend on the intrinsic molecular parameters of the BCP such as the solubility, the relative volume fraction and the length of the blocks.

The degree of complexity of the self-assembly process is enhanced when one block of the di-BCP is able to crystallize. While the crystallization of BCPs in melt, bulk and thin films has been intensively studied and is well-established [18–31], the crystallization behavior of BCPs in solution still presents many unanswered questions, and the fundamental understanding of the self-assembly mechanism of semicrystalline micelles is far from complete. For the semicrystalline BCPs where the insoluble block is able to crystallize in a selective solvent, the crystal packing forces play a dominant role in determining the morphology of the core objects that are formed [16]. Crystallization-driven self-assembly (CDSA) has emerged as a powerful method for block copolymer architecture manipulation. Recent advances in BCP synthesis, enriched by the development of self-assembly schemes, provided access to a rich collection of semicrystalline BCP micelles. A variety of morphologies consisting of crystalline core-forming micelles has been lately reported for different di or tri-BCP [17,32–67].

In this article, we focus our attention on recent developments in the fabrication and manipulation of semicrystalline diblock copolymer micelles. In Section 2, we discuss self-assembly approaches and mechanisms which result in the formation of micelles with a crystalline-core. Here, the main focus remains on the large variety of architectures available from semicrystalline BCPs and the role played by the crystallization process in the structure development. Also, we illustrate different morphological transitions encountered

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by semicrystalline BCP micelles, where the competition between the crystallization of the micellar core and the stretching of the corona block results in unique and interesting micellar structures. Section 3 presents the directed self-assembly of colloidal particles through an underlying controlled crystallization process of micelles with a crystalline corona that leads to the development of hybrid inorganic-organic materials. Finally, some perspectives in the field of semicrystalline BCP micelles are briefly discussed.

2. Design of crystalline core-micelles: general pathways of crystallization-driven self-assembly (CDSA)

2.1. General aspects of semicrystalline di-BCP micelle formation: guiding assembly in selective solvents

In the current section we present a brief outline of the factors that govern semicrystalline di-BCP micelle formation, and we summarize various self-assembly strategies applied to develop a large number of unique and interesting morphologies as illustrated in Fig. 1.

In solution, the interactions between the solvent and the different blocks dictate the ability to form well-defined micellar structures. Often, the formation of semicrystalline BCP micelles can be viewed as a two-step self-assembly process. Micelles with an amorphous insoluble core-forming block develop by minimizing their contact with the solvent, and then start to crystallize in a second step, giving rise to the final micellar structure. As a general rule, the geometry and degree of order of these architectures depend not only on the molecular characteristics of the BCP, but also on the ratio between the insoluble and the soluble blocks. As crystallization takes place in the insoluble micellar core, the initial morphology is either preserved or a morphological transformation/development into a novel structure is triggered through a reorganization process as shown in Fig. 1. Therefore, the structure development of BCPs in solution will depend on two competing

self-organizing mechanisms: microphase separation and crystallization.

From the theoretical point of view, Vilgis and Halperin established a scaling analysis for the morphology development of semicrystalline di-BCPs in selective solvents in which the insoluble block can crystallize [16]. According to this model, the insoluble and crystallizable block forms crystals through adjacent folds within the core, and a sharp interface divides the crystalline core from the solvent-swollen corona. The corona chains are grafted to the core at a spacing that depends on the number of folds per core block. Thus, the response to strong corona chain repulsion is a large number of thinner folds of the crystallizable core-forming block. The core crystallinity affects the equilibrium state of the resulting structure as follows: in a first step crystallization determines the packing mode of the core block (by inducing chain folding), and sets the relationship between the grafting density of the amorphous block and the core geometry. As a direct consequence, the crystallization gives rise to two different surface tensions associated with the chain fold. The first one arises from the interfacial tension in the fold plane, while the second characterizes the lateral interfacial tension at the edge of each crystal. From this model, the most common morphology expected is a lamellar structure where the corona chains protrude from both faces. In the case of a very long soluble block, cylindrical or even star-like micelles are expected (see Fig. 1a). Because the core is formed by adjacent folds of the crystalline polymer, the core of the semicrystalline micelles does not have a circular cross section but is rather formed by an end-to-end packing of a rectangular unit cell.

Experimentally, different approaches have been employed for coil-crystalline di-BCPs in order to obtain semicrystalline micelles as schematically summarized in Fig. 1. Here, crystallization is the main driving force for solution self-assembly of the di-BCPs. In this way, a large variety of morphologies were prepared by adjusting parameters such as the crystallization conditions, the micelle concentration or the volume ratio between insoluble and soluble

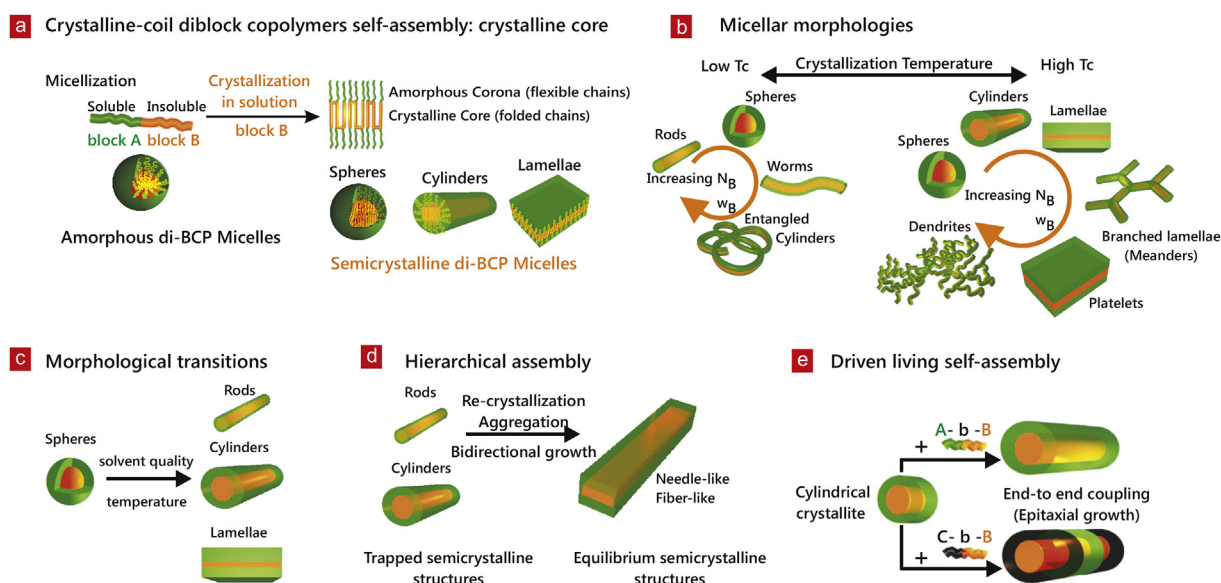


Fig. 1. Different self-assembly strategies to prepare semicrystalline micelles with a crystalline core: a) Schematic illustration of the fabrication of semicrystalline BCP micelles from amorphous micelles in solution where the chains of the core-forming block undergo crystallization through a folded-chain structure as predicted by Vilgis and Halperin [16]. The A and B diblock copolymer, is depicted as a simple two-color chain for simplicity. Typical structures of semicrystalline BCPs micelles: spheres, cylinders and lamellae. b) Representative morphologies formed from PB-*b*-PEO in *n*-heptane as a function of molecular size and composition. The concept of this figure originates from Ref. [17] c) By altering the solubility of the corona-forming blocks in the solvent, the resulting micellar morphology can be further tuned. d) Structures formed from kinetically trapped semicrystalline micelles resulting from the re-crystallization and aggregation of the intermediate structures. e) Micellar morphologies obtained by epitaxial crystallization process, where the addition of extra crystallizable BCP-unimers to the highly reactive crystal surfaces that are present in solution leads to a living type extension of the micellar structure. This concept is discussed in details in Section 2.5.

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